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SECONDARY REACTIONS OF PRIMARY PRODUCTS OF THE FISCHER–TROPSCH SYNTHESIS PART II. THE ROLE OF PROPENE

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Summary

Co-feeding experiments have shown that propene can re-participate in the synthesis reaction by simultaneous bond fissions and formation. The resulting catalytic behaviour depends on the propene concentration. At low concentrations (1 mol% propene), bond fission is very pronounced and results in a substantial increase in the rate of methane formation. At higher concentrations (5 mol% propene), no bond fission is observed and synthesis participation results in a slightly higher synthesis activity. At still higher concentration (10 mol% propene), synthesis activity is suppressed by site occupancy by propene.

Propene acts as a scavenger of surface hydrogen, thereby causing a propene concentration-dependent increase in the olefin selectivity and a decrease in the methane selectivity.

Introduction

Secondary reactions of the initial products during the synthesis process have an important influence on the overall product distribution. We therefore have investigated secondary reactions of several products. In the first paper in this series [1], we have given an overview of the relevant literature and, in addition, we reported on a study of secondary reactions of ethene. Propene is known to be much less reactive in secondary growth reactions on all three Fischer–Tropsch-active metals: iron [2], cobalt [3] and ruthenium [4], its rate of incorporation being only 10 - 25% of that of ethene.

In addition to incorporation, added alkenes can also undergo bond fission. The rate of hydrogenolysis increases with increasing chain length [5]. Studies involving labeled alkenes [2] showed an isotopic effect between the α-carbon atom of 1-hexadecene and adsorbed C_1 species, which

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participate in propagation as evidenced by observed radioactivity in the light products.

Eckerdt and Bell [6] report that olefin additives with ruthenium catalysts act as scavengers of surface intermediates to form alkylated products. These results are consistent with results by Pichler and Schulz [7] and Emmet and coworkers [8 - 10] on iron and cobalt catalysts. Results obtained by Kobori *et al.* [11] with ruthenium catalysts and Schulz *et al.* [2] with iron and cobalt catalysts show that hydrogenolysis and incorporation take place simultaneously and that carbon from the olefins is incorporated randomly in the reaction products, indicating that the scavenger effect of added alkenes [6] can be very small.

In addition, propene can undergo dimerization, as evidenced by a sharp increase observed in the concentration of 2-methylpentene and 2-methylpentane [2] or of internal hexenes [4] when propene was added to the synthesis gas stream.

Many of the available literature data have been acquired at atmospheric pressure. However, synthesis pressure is known [2] to have a considerable influence on secondary reactions of primary products. Our studies on secondary reactions of primary products are therefore carried out under conditions similar to those prevailing in industry. Particular attention has been given to methane selectivity, olefin selectivity and overall synthesis activity. This communication reports on the role of propene.

Experimental

The catalyst used in this study was prepared by partial combustion of iron citrate complexes [12]. The oxidic catalyst precursor was crushed and screened to particle sizes in the range of 0.2 to 0.6 mm and reduced at a pressure of 300 kPa hydrogen at a flowrate of 1.6×10^{-6} m^3 s^{-1} for 3 - 5 h at 433 K and subsequently for 16 - 20 h at 573 K.

The catalytic behaviour was evaluated in a fixed bed microreactor system [13] based on a concentric tube design [14]. The product was analyzed by means of an on-line gas chromatographic data system [15 - 17]. The reaction conditions employed were pressure of 2.0 MPa, temperature of 543 K and a flow (VHSV = 1000) of synthesis gas with mol ratio H_2:CO = 0.5.

Synthesis gas containing propene (1, 5 or 10 mol%) was prepared in and fed from a gas mixing–feeding station [18].

Synthesis experiments were always started with pure synthesis gas only. When steady-state conditions had been reached, the pressure was lowered to 0.1 MPa and immediately raised to the working pressure of 2.0 MPa using propene-containing synthesis gas. This procedure permitted rapid replacement of pure synthesis gas with that in which propene was present. Before termination of experiments the reverse procedure was followed, in order to ascertain whether any observed changes in the catalytic behaviour under propene co-feeding conditions were reversible.

Results and discussion

In presenting the results, use is made of relative units of activity and selectivity, the base data relating to experiments in which no co-feed was used. The results presented have been calculated on the assumption, as made by others [4], that the rate of C_3-production under conditions when co-feed was used, was equal to that observed under normal conditions.

Synthesis activity is expressed as the conversion of single carbon units in the carbon monoxide-plus-propene pool to hydrocarbons. Methane selectivity is expressed as the mass percentage of methane in the product (corrected for unconverted propene and propane formed by hydrogenation of co-fed propene). Olefin selectivity is expressed as the mass percentage of alkenes in the C_2-C_5 hydrocarbon fraction (corrected for unconverted propene and propane formed by hydrogenation of co-fed propene).

Steady state conditions were reached after about 100 ks on stream. The product distributions before and after co-feeding were identical.

Conversion of carbon monoxide to hydrocarbons (before and after co-feeding) was ~10%. The rate of hydrocarbon synthesis was *ca.* 7 μmol s^{-1} g cal^{-1}.

Transient behaviour with 1 mol% propene addition

When the feed was changed from pure synthesis gas to propene-containing synthesis gas, a drop in the synthesis activity and the methane selectivity, together with an increase in the olefin selectivity was observed (Fig. 1). The decrease is attributed to a disturbance of the steady state

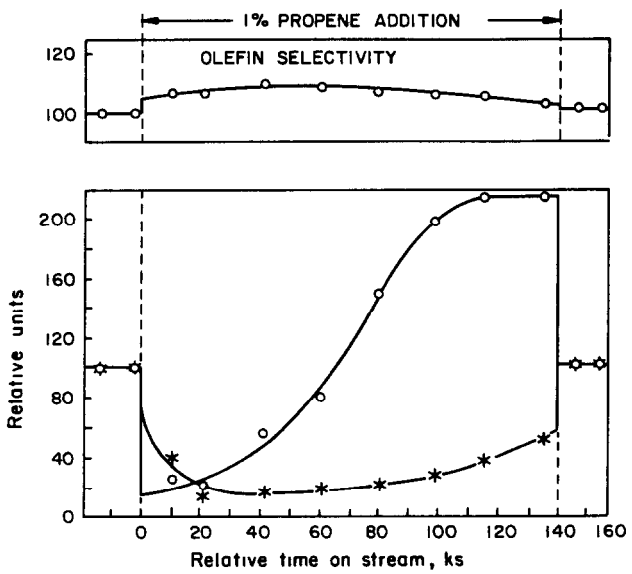

Fig. 1. Influence on the catalytic behaviour of co-feeding propene at a concentration of 1 mol%. (★) Activity, (○) methane selectivity.

situation by the sudden sharp increase in propene concentration. In principle, the decrease in methane concentration could be explained by any one or a combination of four different effects:

(i) secondary reaction of methane with propene, resulting in a lower methane selectivity;

(ii) large-scale participation by propene in the synthesis reaction, thereby decreasing the methane concentration at the percentage level, although the rate of methane formation remains constant;

(iii) inhibition of methane formation by the presence of adsorbed propene;

and

(iv) large-scale participation by propene in the hydrocarbon synthesis by reaction with C_1-intermediates which are also responsible for methane formation, thereby reducing the surface concentration of these intermediates and hence the rate of methane formation.

The highly unlikely occurrence of effect (i) was discounted from the results of a simple experiment. The addition of an equimolar stream of methane to the propene stream did not result in a significant decrease in the propene concentration, nor was a significant increase in synthesis activity observed.

The occurrence of effect (ii) can also be easily discounted. Since the rate of methane formation remains unaffected by propene addition, co-feeding will result in a dilution of the product obtained under standard conditions by the products derived from the added propene. Thus the methane selectivity observed when co-feeding 10 mol% propene should have a value of 50% of its standard value. However, a significantly lower value is found. Similar differences are observed with the other two propene concentrations. In addition, the effect presupposes a considerable increase in overall synthesis activity and this is not the case. Consequently, the observed results are not caused by a dilution effect, but genuine changes in the rate of methane production.

Effect (iii) is much more likely to occur. If propene is adsorbed in large amounts under synthesis conditions, it will act as a surface-hydrogen scavenger, as reflected in the observed increase in olefin selectivity. The scavenging effect of propene is less pronounced than that observed with ethene, because only 35% of the C_3 species in our reaction product was hydrogenated, as opposed to 60% of the C_2 product when ethene was co-fed [1]. A decrease in the concentration of surface-hydrogen will affect the product distribution.

If we accept a simple chain-growth mechanism as proposed by Kugler [19], then hydrocarbon synthesis is initiated by the formation of an activated single carbon intermediate, as shown in Fig. 2. This intermediate either follows Anderson–Schulz–Flory polymerization kinetics or undergoes a hydrogenation step to produce methane. Under conditions that limit the availability of active surface hydrogen [19], there is a decrease in the rate of formation of methane. Since the desorption of C_{2+} hydrocarbons as

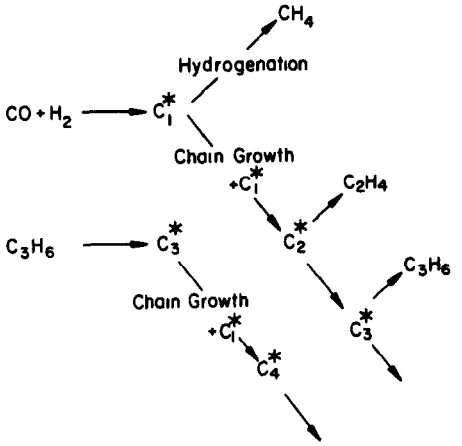

Fig. 2. Simple mechanism of hydrocarbon synthesis by either polymerization or hydrogenation of a C_1-intermediate [19], showing additional synthesis initiation by propene.

alkenes does not require the participation of active hydrogen, the rate of formation of higher hydrocarbons need not be affected. We suggest that a similar effect is in operation in the present case, albeit much less pronounced than that observed with ethene as a co-feed. In the latter case a decrease of *ca.* 50% is observed in the rate of methane formation [1], even at a co-feed concentration of 5 mol%.

Effect (iv) is not likely to have a large influence, because synthesis initiation or propagation by propene is likely to drastically affect the concentration and/or formation of C_2 products, and no large deviations are observed. However, large-scale synthesis initiation by propene is likely to effect the formation of methane. Following Kugler [19], we believe that, under synthesis conditions without co-feed, the C_1 intermediate in the synthesis reaction scheme presented in Fig. 2 can (a) undergo hydrogenation to form methane, (b) initiate hydrocarbon synthesis or (c) propagate synthesis by reacting with either adsorbed propene, growing hydrocarbon chains or itself. If propene is present in large amounts, its reaction with the C_1 intermediate will largely suppress any of the other reactions involving the intermediate, including methane formation. However, propene is known [2 - 4] to participate in the synthesis to a limited extent only, and large scale participation is unlikely in the present case because of the suppressed synthesis activity. Although C_1 intermediate scavenging is not likely to occur to any large extent, a contribution from this effect cannot be excluded.

In conclusion, both hydrogen scavenging and intermediate scavenging by propene are thought to be responsible for the suppression of methane formation. The observed increase in olefin selectivity is, by its very nature, most likely to be effected by hydrogen scavenging. Finally, the large surface presence of propene is likely to be responsible for the suppression of overall synthesis activity by site occupancy.

Propene hydrogenolysis

After the initial disturbance of the hydrocarbon synthesis by propene, an increase is observed in the methane selectivity and overall synthesis activity (Fig. 1). We suggest that propene hydrogenolysis is responsible. Ethene hydrogenolysis did not occur to any noticeable extent [1] under identical synthesis conditions but with ethene as co-feed. However, hydrogenolysis is known to occur much more easily with propene than with ethene [2, 5]. Products from propene hydrogenolysis have a radical character [5]. Therefore, they have a much higher reactivity than propene itself. As a consequence, propene hydrogenolysis could result in a substantial increase in both the overall synthesis activity and the formation of methane.

It is not uncommon with reactions involving radicals, that the rate of reaction is initially relatively slow, but increases gradually afterwards. A similar observation is made for the rate of methane formation, which increases substantially with increasing time on stream, despite the opposite effect of hydrogen-scavenging by propene which must be in operation simultaneously. The overall synthesis activity increases to a lesser extent than the methane selectivity, suggesting that the majority of the propene fragments is converted to methane, in contrast to reports [2] that only 10% of the hydrogenolysis products appear as methane.

The high rate of methane formation indicates a relatively high rate of hydrogenolysis, suggesting that hydrogenolysis takes place on a relatively large fraction of the surface. This, in turn, suggests substantial site occupancy by the additional propene, resulting in fewer sites than normal being available for the adsorption of synthesis gas. Thus, synthesis activity remains at a lower than normal level, despite the fact that hydrogenolysis products contribute to the final product.

Transient behaviour of chain growth

When the feed was changed from pure synthesis gas to propene-containing synthesis gas, a temporary drop in the synthesis activity (Figs. 1 and 3) and chain-growth probability (Fig. 4) was observed. The decrease is attributed to a momentary disturbance of the steady state situation. The disturbance disrupts hydrocarbon synthesis and only intermediate short-chain hydrocarbon entities, formed on the surface before the disturbance, appear in the product, as evidenced by the lower growth probability observed.

Apparently synthesis is soon resumed, as indicated by an observed increase in activity and growth-probability. However, the increase in both parameters is only observed with the lower co-feed concentrations; at 10 mol% only a very low level of activity is maintained.

The product spectrum obtained from the catalytic hydrogenation of carbon monoxide almost invariably follows a mathematical relationship known as the Anderson–Schulz–Flory (ASF) product distribution statistics [20] which can be expressed mathematically as:

$$\Phi_n = \Phi_1 P^{n-1}$$

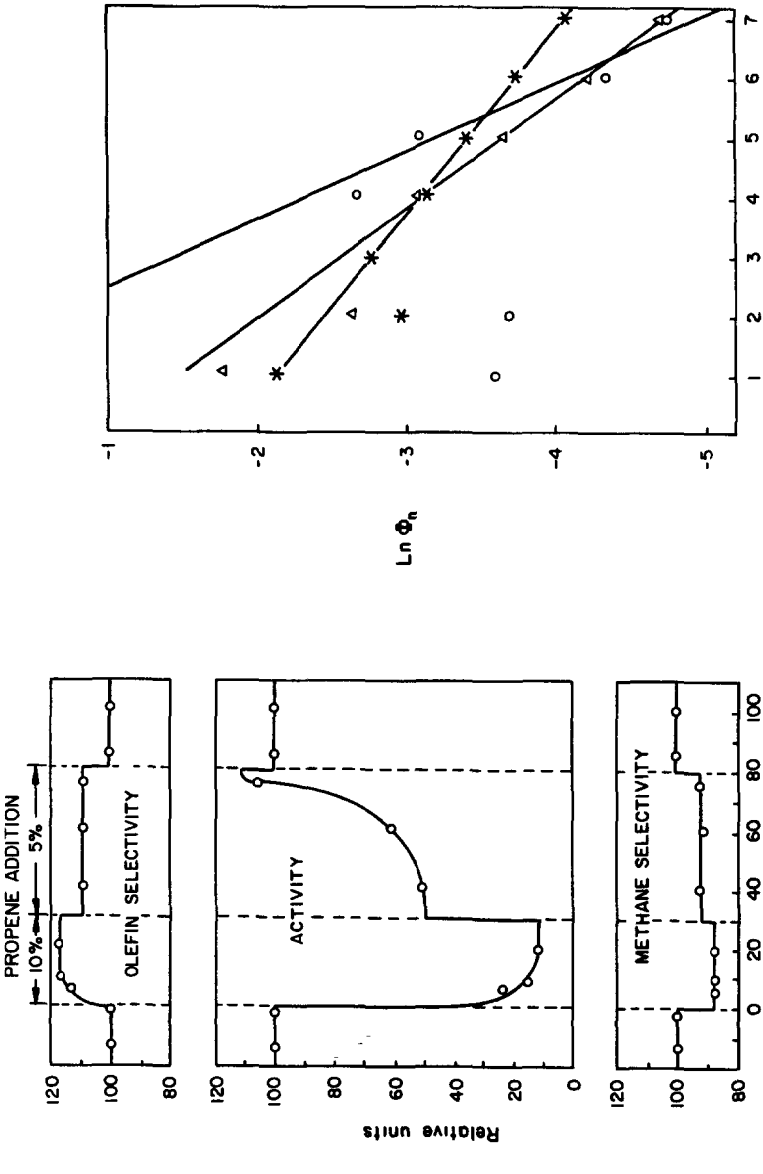

Fig. 3. Influence on the catalytic behaviour of co-feeding propene at concentrations of 5 and 10 mol%.

Fig. 4. ASF plot of the product distribution obtained from synthesis gas containing 1 mol% propene at different times on steam, and pure synthesis gas in the control experiment. (○) t = 10.3 ks, P = 0.43; (△) t = 96.9 ks, P = 0.58; (✱) control, P = 0.72

where Φ_n and Φ_i are the number of moles of a hydrocarbon with carbon number n or i, respectively, and P is the probability of chain growth. The value of P can readily be determined from the slope of ASF plots where Φ_n is plotted as a function of n (Fig. 4).

Immediately after changing the feed, ASF statistics were not adhered to in the $C_1 - C_2$ hydrocarbon fraction (Fig. 4), but heavier hydrocarbons exhibited normal ASF behaviour. The value of P decreased initially considerably, from a value of 0.72 before co-feeding to 0.43, gradually to increase again to 0.58 after 96.6 ks of co-feeding.

If propene participates in the synthesis, either as an initiator or as a propagator, then the product can be divided into two parts: one part is formed from synthesis gas only and the other part contains the products from propene. When hydrogenolysis does not occur, propene can only contribute to the C_{4+} hydrocarbon fraction. In that case only the C_{4+} hydrocarbon fraction is predicted to follow ASF statistics, while the concentration of the $C_1 - C_2$ fraction is expected to be much lower, being formed from synthesis gas only. This is indeed observed (Fig. 4). Since the building blocks are now not only C_1 species, a change in the growth probability is conceivable, but not necessary.

The low value of P ($P = 0.42$), observed immediately after the switch to mixed feed, indicates that the average number of carbon atoms of the product is $(1 - P)^{-1} = 1.75$. Even when allowance is made for the much lower concentration (than predicted by ASF statistics) of the $C_1 - C_2$ fraction, it appears that propene is initially incorporated into most of the product. This agrees well with the expectation that at the moment of feed change, the only products are desorbing short-chain intermediates and reaction products from reaction of those intermediates with propene. Moreover, the strong suppression of methane suggests C_1 intermediate scavenging, which in turn indicates considerable synthesis participation by propene, although the synthesis activity itself is at a very low level.

Transient behaviour with 10 mol% propene addition

When propene is co-fed at a concentration of 10 mol%, a marked increase in the olefin selectivity is observed (Fig. 3), indicating surface-hydrogen scavenging. Synthesis activity is more substantially suppressed than observed with 1 mol% propene addition, suggesting a stronger competition for surface sites. Suppression of methane occurs, but to a much lesser extent than observed with the lower propene concentration. Because of the rather small suppression, we suggest that the suppression is caused by hydrogen-scavenging only, and that no or very little C_1 intermediate scavenging or propene hydrogenolysis occurs. In contrast to the observation with 1 mol% propene addition, the decrease in activity was not only sharp, it was also sustained.

Co-feeding of propene at a concentration of 0.3 mol% has been reported [2] to result in propene hydrogenolysis, while at concentrations of 5 mol% or higher no change in the rate of methane selectivity was

observed [4]. It is conceivable that propene hydrogenolysis is restricted to low propene concentration. The absence of propene hydrogenolysis at higher propene concentrations could perhaps be attributed to a lack of available surface sites for the hydrogenolysis reaction [2, 21], due to the large propene presence. However, regardless of the reason why, the large differences observed in the catalytic behaviour when co-feeding 1 or 10 mol% propene can be explained by both the observed propene-concentration-dependent hydrogenolysis reaction and the concentration-dependent competition for surface sites.

No influence of the co-feed on the product distribution was observed. ASF statistics were adhered to throughout (Fig. 5). The insensitivity to propene addition at 10 mol% is attributed to the absence of propene hydrogenolysis which is observed at lower propene concentrations.

Transient behaviour with 5 mol% propene addition

Once the catalytic behaviour observed when co-feeding 10 mol% propene had reached steady state conditions, the feed was changed to synthesis gas containing 5 mol% propene. The activity increased immediately to a level having about the average value of those obtained with 0 and 10 mol% propene (Fig. 3). Simultaneously similar changes occurred in the selectivity. The olefin selectivity decreased with the methane selectivity.

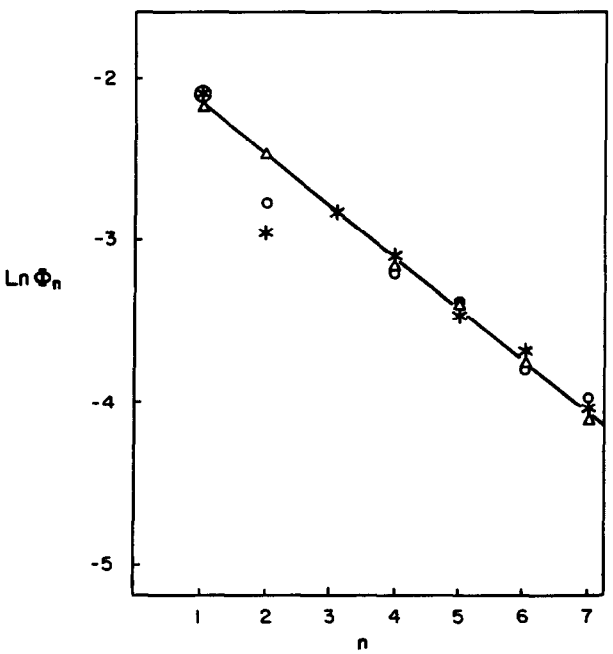

Fig. 5. ASF plot of product distributions obtained from synthesis gas containing (★) 0, (○) 5 or (△) 10 mol% propene.

Both selectivities changed abruptly to levels having about the average value of those obtained with 0 and 10 mol% propene.

The immediate changes in the catalytic behaviour indicate that at the moment of feed change a significant disruption occurs in the hydrocarbon synthesis. We have already suggested that at the high propene concentration of 10 mol% severe competition exists between synthesis gas and propene for adsorption sites, resulting in a much depressed synthesis activity. As soon as the propene concentration is lowered, the catalytic behaviour is observed to change to levels having about the average value of those obtained with 0 and 10 mol% propene. The proportionality between the change in catalytic behaviour and the concentration of co-feed indicates that the competition for adsorption sites has a dominating effect on the catalytic behaviour.

After the immediate changes, the selectivity levels were maintained, but the activity increased gradually to a level slightly above that normally observed (Fig. 3). The immediate change to an intermediate level followed by a more gradual change indicates that two effects are involved. The first and immediate change in activity is already attributed to the immediate change in competition for adsorption sites. However, this does not yet mean an immediate change in site occupancy. The latter is thought to constitute the second effect. The large surface presence of propene, which had kept the activity at the intermediate level, now slowly decreases by desorption and incorporation. The resulting gradual change in site occupancy allows increasing availability of surface sites for synthesis gas. This line of thought is substantiated by the observed acceleration in the rate of hydrocarbon synthesis.

No influence of the co-feed on the product distribution was observed and ASF statistics were adhered to throughout (Fig. 5). This observation supports the other indications that no substantial propene hydrogenolysis occurs at higher propene concentrations.

Influence of propene addition on the yield of C_2 product

Earlier [1] we have shown that ethene can readily initiate synthesis on adsorption. Under normal conditions a fraction of the primarily formed ethene re-adsorbs to initiate chain growth. Such behaviour is reflected in the general observation with iron catalysts that the C_2 product concentration is often lower than predicted by ASF statistics (*e.g.* the control experiments in Figs. 4 and 5), particularly under elevated synthesis pressure.

When propene is added to the synthesis gas stream, re-adsorption of ethene is hampered by the large surface presence of propene, reparticipation of ethene in the synthesis is suppressed and the yield of C_2 product comes in line with ASF statistics (Figs. 4 and 5). This line of thought is supported by the observation that the yield of C_2 product comes increasingly in line with ASF statistics when the propene concentration in the reactant stream is increased. The yield of C_2 product reaches the statistical concentration when 10 mol% propene is added (Fig. 6). At this co-feed concentration, propene appears to inhibit any re-adsorption by ethene.

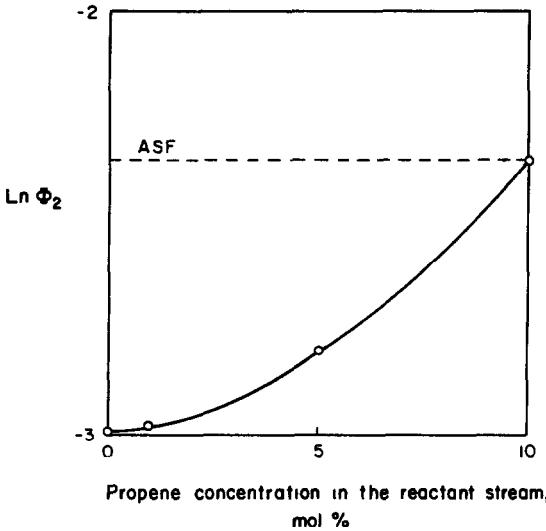

Fig. 6. Effect of the propene concentration on the relative yield of C_2 product predicted by ASF statistics at the higher propene concentration. Because of the non-ASF distribution at 1 mol% propene, the yield of C_2 product is expressed relative to those products that are formed from synthesis gas only.

It could be argued that the relatively high yield of C_2 product observed with 1 mol% propene addition is due to propene hydrogenolysis. However, this is unlikely since hydrogenolysis does not occur at higher propene concentrations, and the yield of C_2 product is observed to increase with increasing propene concentration (Fig. 6).

Rate of propene incorporation relative to that of ethene

The results indicate that the rate of propene incoporation is lower than that of ethene, in line with reports in the literature for iron [2], cobalt [2, 3] and ruthenium catalysts [4]. The lower rate is also reflected in the observation that the yield of C_3 product is normally in line with the statistics and is not influenced by butene addition [22]. This observation is in contrast to the observations of the yield of C_2 product, which is usually lower than that indicated by ASF statistics, and only comes in line with the statistics when large amounts of propene are co-fed. As a result of the much lower rate of propene incorporation, relative to that of ethene, the surface concentration of propene remains high enough to severely inhibit absorption of synthesis gas and hence synthesis initiation; and thus the overall rate of synthesis decreases substantially, in contrast to the observation made with ethene as a co-feed [1].

Effect of propene concentration on the catalytic behaviour

The observed influence of the propene concentration on the catalytic behaviour has been shown to be the due to two effects· competition for

surface sites and propene hydrogenolysis. Because of the competition for surface sites between hydrogen, carbon monoxide and propene, there is a trend for proportionality between the partial pressure of propene and several aspects of the catalytic behaviour, as discussed before. An increase in the propene concentration in the feed is associated with a proportional increase in the site occupancy by propene, resulting in increasingly hampered secondary hydrogenation of primary olefinic products and proportional scavenging of surface hydrogen. Consequently, a proportional increase in the olefin selectivity is observed (Fig. 7).

Similarly, an increase in the concentration of propene is associated with a proportional increase in the scavenging of surface hydrogen and possibly C_1 intermediates, resulting in a proportional decrease in methane selectivity. However, it should be noted that the proportionality is not valid at 1 mol% propene because of the additional operation of the second effect: propene hydrogenolysis. This second effect does not influence secondary hydrogenation or hydrogen scavenging and was therefore not observed in the behaviour of the olefin selectivity.

Operation of the first effect alone shows a slight increase in synthesis activity at propene concentrations up to ~5 mol% because of limited propene incorporation. At higher propene concentrations, increased site occupancy inhibits synthesis and the activity decreases with increasing

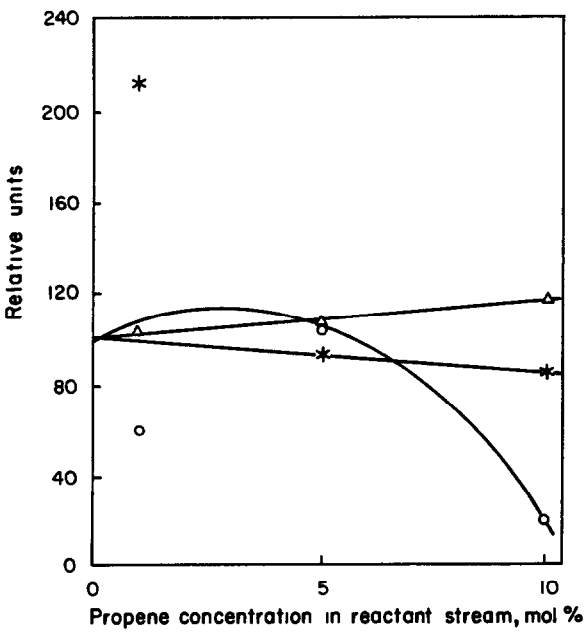

Fig. 7. Influence of the propene concentration in the reactant stream on the catalytic behaviour under steady state conditions. (○) Activity, (△) olefin selectivity, (★) methane selectivity.

propene concentrations. The additional occurrence of propene hydrogenolysis at low propene concentrations suppresses synthesis, and a lower than expected activity is observed (Fig. 7).

Implications for the mechanism

We have shown that ethene participates in the hydrocarbon synthesis with a much higher rate than propene, in line with observations involving entirely different catalysts [2 - 4]. The implication for the mechanism is that under normal conditions the primarily formed alkenes re-adsorb and re-participate in the synthesis. As discussed before, because of the high rate of participation for ethene, the yield of C_2 products is normally lower than predicted by ASF statistics. While propene does participate to some extent, the yield of C_2 products is normally always in line with the statistics. Re-participation is therefore indicated for all C_{3+} product.

It has been reported [2] that higher alkenes, *e.g.* C_{14}, can also partake in secondary chain growth, and that the rate of incorporation decreases with increasing chain length. The result is a slightly lower concentration of light products in the final product than expected on the basis of ASF statistics of the primary synthesis. It is quite conceivable that secondary growth does not affect the adherence to ASF statistics, but a lower value of P is indicated.

In contrast to reports in the literature [2, 4, 23] no evidence of dimerization or similar alternative routes was observed.

In addition to secondary growth, alkenes are also subjected to hydrogenolysis, and increasingly so with increasing chain length [5]. Part of the hydrogenolysis product is converted to methane and other low-chain hydrocarbons, resulting in a higher than expected selectivity for those products. Another part of the hydrogenolysis product is incorporated in the higher product, giving it a slightly higher concentration in the final product than expected on the basis of ASF statistics of the primary synthesis.

In agreement with Kobori *et al.* [11], we contend that both effects, incorporation and hydrogenolysis, occur simultaneously. They are largely working in opposite directions, but are unlikely to be masking each other's influence on the product distribution. Both effects contribute to a change in the ASF statistics, but are not likely to change the overall ASF-adherence of the product, because in practice adherence is generally observed. However, both effects will have their influence on the value of P and it is very unlikely that the observed value will reflect the primary chain growth. It is remarkable that the distribution of the final product mixture, resulting from a combination of hydrogenolysis of primary and secondary products, in addition to primary and secondary growth, is normally well described by ASF statistics, with ethene as the only exception.

Moreover, in further agreement with Kobori *et al.* [11], we found no indications of intermediate scavenging as proposed by Eckerdt and Bell [6].

Because the secondary reactions do not affect the catalyst as such, all changes in the catalytic behaviour under co-feeding conditions are predicted to be reversible, as is indeed observed.

One of the secondary reactions of propene contributes to chain branching. This subject is not discussed here, because we have discussed chain branching in Fischer–Tropsch synthesis in depth elesewhere [24].

Conclusions

The results obtained from this study have shown that propene can re-participate in the hydrocarbon synthesis, but to a much lower extent than observed with ethene. At low propene concentrations (1 mol% of the reactant stream) propene undergoes severe hydrogenolysis, resulting in inhibited synthesis and enhanced methane production. At higher propene concentrations no hydrogenolysis is observed, and at increasingly higher concentrations synthesis activity is more and more suppressed, which is attributed to site occupancy by propene.

A slight methane suppression and enhanced olefin selectivity are observed at higher propene concentrations, ascribed to surface hydrogen scavenging by propene. The yield of C_2 product increases when the propene concentration is increased, ascribed to enhanced inhibition of re-adsorption and re-participation of propene in the synthesis.

The data presented show that propene is involved in a rather complex network of reactions, but give insufficient information to allow any conclusion about the particular synthesis mechanism involved. Future studies will help to achieve a more detailed picture of the hydrocarbon synthesis mechanism.

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